Study optical properties for pbS thin films before and after irradiation by CO_2 laser

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Abstract
In this study, Lead sulphide (PbS) thin films were deposited on glass substrates using the thermal vacuum evaporation technique at pressure 10^{-6} torr. The prepared films were annealed to 200°C by using oven under vacuum with pressure 10^{-2} torr then the samples irradiated by CO_2 laser of power (1 watt) and wavelength (10.6) μm at distance (10 cm) from the source for (5 sec). The optical characteristics of the prepared thin films have been investigated using IR spectrophotometer. Optical constants such as absorption, reflection, absorption coefficient (α), Band gap energy (E_g), extinction coefficient (K), refractive index (n), and complex dielectric constants (ε_r&ε_i) were evaluated from transmission spectra. The results show that the laser irradiation cause decreasing in transmittance, reflection, band gap energy, refractive index and in the real part of dielectric constant while increasing in the absorption, extinction coefficient and imaginary part of dielectric constant, in the investigated region .

Keywords : PbS, thin film, optical properties, energy band gap and laser irradiation .

Introduction

In the recent years there has been increased interest in the use of thin film polycrystalline semiconductors, and has found many applications in various electronic devices. These materials are produced in the crystalline and polycrystalline forms and used as detectors, emitters, as well as solar control coatings. The IV–VI compounds often named as lead salts have been considered as the most attractive semiconductors, because of their various applications in the infrared technology [1]. As an important IV-VI group semiconductor, lead sulphide (PbS) is an important direct narrow band gap semiconductor material (≈ 0.41 eV at room temperature), and has been widely used in many fields such as Pb^{2+} ion-selective sensors, IR detector, photography and solar absorption [2-4].

Laser crystallization of thin films on glass is widely used to improve the electronic transport. In the production of flat panel displays, laser crystallization increases the carrier mobility in thin film transistors. Suitable laser intensity profiles in combination with multiple scanning sequences have been used to reduce the number of grain boundaries [5] .

Laser crystallization appears to be more promising compared to the thermal crystallization as it does not damage the glass substrate and that almost all of the laser energy is directly absorbed into the PbS film [6]. Many techniques have been reported for the deposition of PbS thin films, these include evaporation, sputtering, chemical bath deposition, spray pyrolysis, electrodeposition, photochemical deposition etc. [1, 7-9]. In the present research, thermal evaporation technique has been chosen for the deposition of pbS thin films. We have studied the influence of CO_2 laser on the optical properties PbS thin films

Theoretical part

The measured transmittance (T) of the sample can be used to calculate the optical absorbance (A), using the relation :

$$A=\log 1/T \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Whereas the reflectance (R) was calculated from the following relation :

$$(A+T+R)=1 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

From the absorbance data, the absorption coefficient α was calculated using Lambert law [13]:

$$\ln (I_o / I) = 2.303\ A = \alpha d \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Where I_o and I are the intensity of incident and transmitted light respectively and d the film thickness.

$$\alpha = 2.303\ A/d \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

The relation between the absorption coefficient and photon energy hυ is given by [14, 15]:

$$\alpha = [A_o (h\upsilon - E_g)^n] / h\upsilon \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

where A_o is a constant related to the effective masses associated with the bands , E_g is the band gap energy , and n is a constant, equal to 1/2 for direct band gap semiconductors.

$$(\alpha h\upsilon)^2 = A_o(h\upsilon - E_g) \quad \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

The Extinction coefficient (K) has been calculated using the well-known relation [18]:

$$K = \frac{\lambda\alpha}{4\pi} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

Where λ is the wavelength of incident beam.

The refractive index (n) is the ratio between speeds of light in vacuum to its speed in material which does not absorb this light. The value of n was calculated from the equation [19]:

$$n = \left[\left(\frac{1+R}{1-R}\right)^2 - \left(K^2 - 1\right)\right]^{1/2} + \frac{1+R}{1-R} \quad \ldots\ldots\ldots (8)$$

The real (ε_r), and imaginary (ε_i) parts of dielectric constants are obtained by using the relations:

$$\varepsilon_r = n^2 - K \quad \ldots\ldots\ldots\ldots\ldots\ldots (9)$$

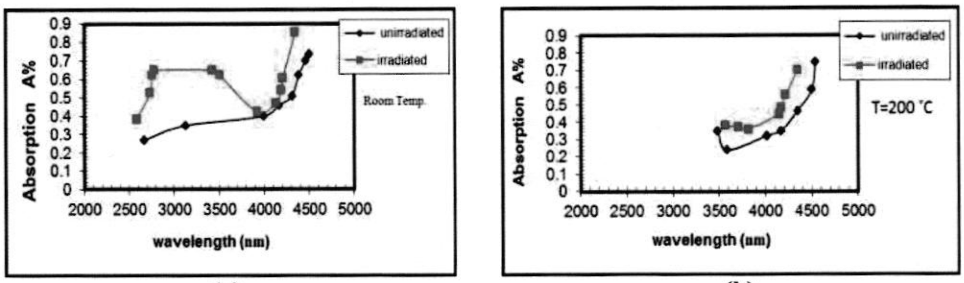
$$\varepsilon_i = 2nK$$

Experimental details

PbS thin films were prepared, from the PbS powder from high purity powders (99.99%) using thermal vacuum evaporation technique type Edwards E 306A on the glass substrate. The substrates were washed with distilled water and with the ethanol and finally the substrates were put in Ultrasonic device for 10 minutes . The deposition chamber was evacuated to pressure 10^{-6} torr, prior to all deposition experiments. Molybdenum boats (Mo) were used in this experiment and the distance between the PbS powder and the substrate was 16 cm. All the samples were prepared at room temperature and they annealed in 200 °C (the sample annealed in different temperature less than 200 °C, but found that 200 °C is the better Temperature) by using under vacuum oven at pressure (10^{-2} torr). The thickness of the prepared films was 300 nm. The thin films were irradiated by using CO_2 laser of power (1 watt) and wavelength (10.6 µm) at distance (10 cm) from the source during (5 sec). For measuring transmittance spectra IR spectrophotometer was used, optical measurements was carried before and after irradiation of the sample before and after annealing at temperature 200 °C .

Results and discussion

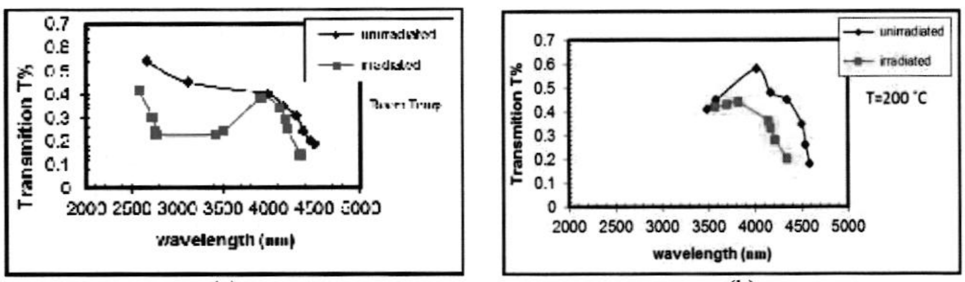
Figure (1) shows the absorption spectra as a function of the wavelength at room temperature and at 200 °C before and after irradiation with CO_2 laser. The absorption value of unirradiated sample increases with increasing wavelength because when photon energy incident equal or greater than the value of band gap energy causes direct transition from valance band to conduction band [10]. Also figure (1) shows increasing in the value of the absorption after irradiation by CO_2 laser, because the irradiation causes some structural defects in the films [11], these may be attributed to the creation of energy states in the region between the conduction and the valance band that will be available for the incident photon to be absorbed.



(a) (b)

Figure (1) The variation of absorption with wavelength (nm) before and after irradiation with CO_2 laser (a) at Room temperature (b) 200 °C

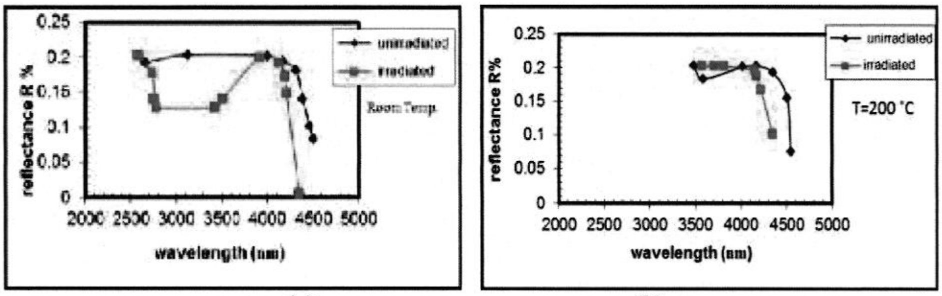
The transmittance spectra as a function of the wavelength at room temperature and at 200 °C before and after irradiation with CO_2 laser are shown in figure (2), which shows that the value of transmittance is high at the short wavelengths and decrease in the long wavelengths. Unirradiate film shows high transmittance compared to irradiated one, this might be attributed to the increased roughness of the irradiated thin films contributed to the drastic decrease of transmittion.



(a) (b)

Figure (2) The variation of the transmittance spectra with wavelength (nm) before and after irradiation with CO_2 laser (a) at Room temperature (b) 200 °C

The reflectance spectra as a function of the wavelength at room temperature and at 200 °C before and after irradiation with CO_2 laser are shown in Figure (3). It can be noted the value of reflectance increase with increasing wavelength until it reaches a maximum value then decreasing. The decrease in reflectance value after irradiation with CO2 laser can be noted because the irradiation might attributed to the increased roughness of the irradiated thin films contributed to the drastic decrease of the value of reflectance [12] .

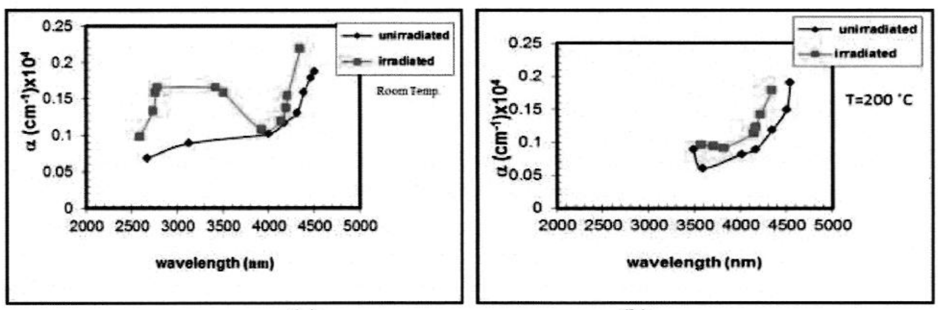


(a) (b)

Figure (3) The variation of the The reflectance spectra with wavelength (nm) before and after irradiation with CO_2 laser (a) at Room temperature (b) 200 °C

A plot of absorption coefficient as a function of wavelength at room temperature and at 200 °C before and after irradiation with CO_2 laser are shown in figure (4), from this figure it can be note that the value of absorption coefficient increase with increasing wavelength before and after irradiation with CO_2 laser this increasing in the absorption coefficient due to increase in the absorption according to equation (4).

The absorption coefficient is found to increase after laser irradiation of the thin film. This is possibly due to the increase in grain size and the decrease in the number of defects [5].

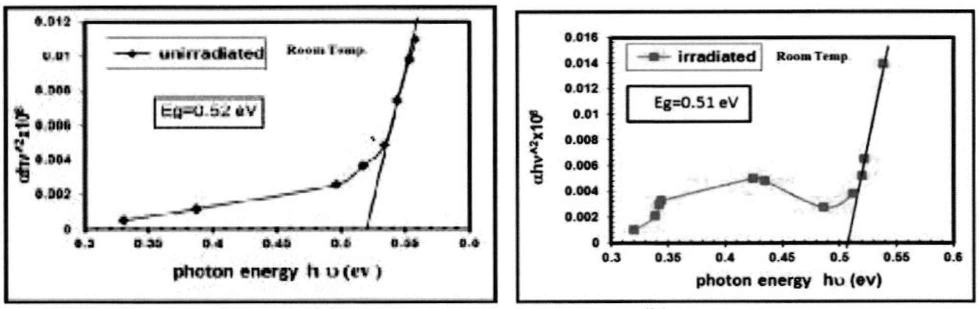


(a) (b)

Figure (4) The variation of the absorption coefficient (α) with wavelength (nm) before and after irradiation with CO_2 laser (a) at Room temperature (b) 200 °C

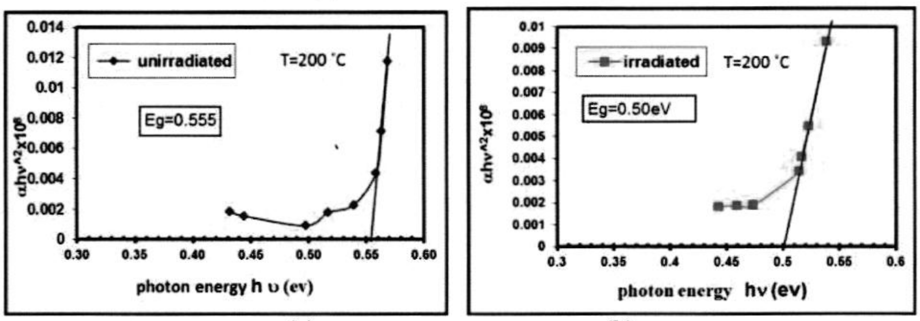
The plots of $(\alpha h\nu)^2$ versus hν are shown in figure (5) and figure (6) for PbS thin films at room temperature and at 200 °C before and after irradiation with CO_2 laser respectively.

The linear nature of the plot indicates the existence of direct transition. The band gap 'Eg' was determined by extrapolating the straight portion to the energy axis at $\alpha = 0$. The decrease in band gap shows that the irradiated film causes a strong 'red shift' in the optical spectra due to sintering of the nanocrystalline into larger crystallites. Lozaca-Morales et al. [16] have reported that while the lattice parameter and grain size are increased, the Band gap energy is decreased. These changes have been attributed to the crystallite size-dependent properties of the energy band gap. The presence of a high concentration of localized states would produce absorption at energy less than the band gap and thereby is responsible for such low values. The weak absorption region at lower energy side is attributed to the presence of intraband transitions at localized states in the gap. The absorption threshold of macroscopic PbS (Eg = 0.41 eV) is 3 μm at room temperature. The absorption threshold of nanocrystalline PbS in infrared is 0.49-0.51 eV, corresponding to nanocrystals of larger size, close to that corresponding to the macroscopic material [17]. The Band gap energy is found to be 0. 52 eV which is slightly different than the bulk material (0.41 eV). It may be due to the fact that the amorphous or nanocrystalline films show band gap energies higher than those of the corresponding bulk materials. The increase in the band gap energy is due the nano-crystalline nature of the PbS film [3]. It is clearly observed in Fig.5 that the optical gap is lowered from 0.52eV before irradiation to 0.51 eV after laser irradiation at Room temperature and lowered from 0.555eV before irradiation to 0.50 eV after laser irradiation at 200 °C. As seen also from Fig.5 and Fig.6 as a result of irradiation, the absorption edge shift to longer wavelengths which confirm the photodarkening. The red shift manifests the fact that Urbach tail light can generate mobile carriers, holes in present pbS thin film.



(a) (b)

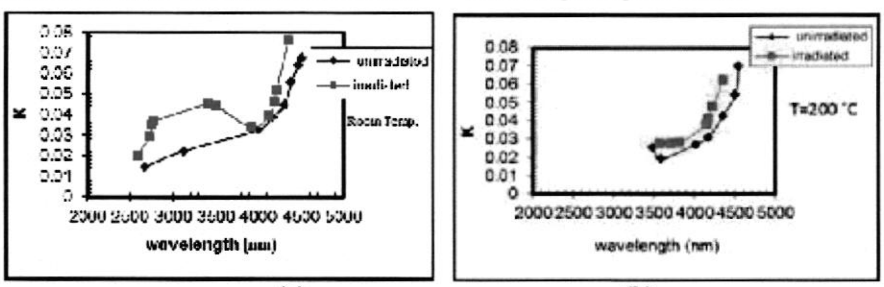
Figure (5) The $(\alpha h\upsilon)^2 \cdot 10^8$ as a function to the photon energy at room temperature (a) before irradiation with CO_2 laser (b) after irradiation with CO_2 laser



(a) (b)

Figure (6) The $(\alpha h\upsilon)^2 \cdot 10^8$ as a function to the photon energy at 200 °C (a) before irradiation with CO_2 laser (b) after irradiation with CO_2 laser

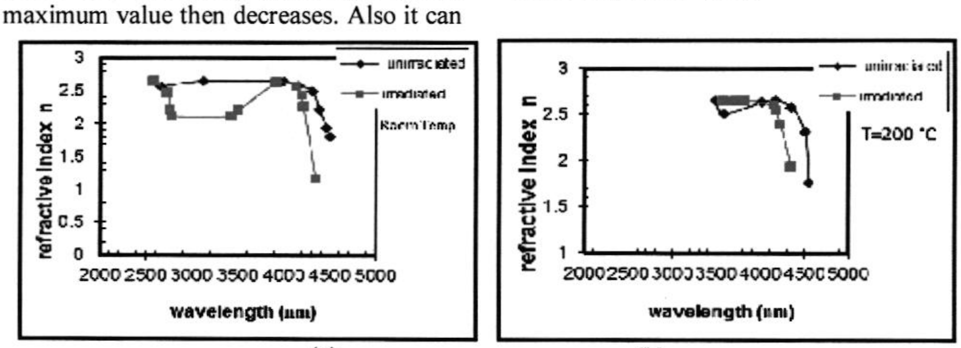
Figure (7) shows the variation of the Extinction coefficient as a function of wavelength at room temperature and 200 °C before and after irradiation with CO_2 laser. It can be observed that the Extinction coefficient increased with increasing wavelength before and after irradiation with CO_2 laser and this behavior is similar to absorption coefficient behavior according to equation (7) .



(a) (b)

Figure (7) The variation of the Extinction coefficient with wavelength (nm) before and after irradiation with CO_2 laser (a) at Room temperature (b) 200 °C

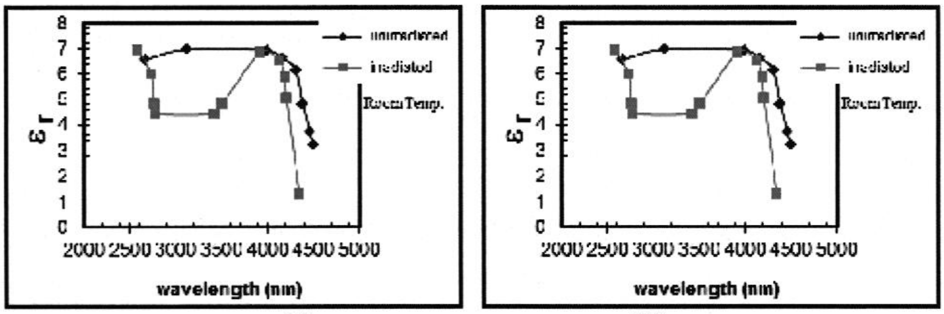
The variation of refractive index with wavelength is shown in figure (8). It is observed that the refractive index increased with increasing wavelength until it reaches a maximum value then decreases. Also it can be noted that the refractive index decreases after irradiation with CO_2 laser, this is similar to behavior of the reflectance value.



(a) (b)

Figure (8) The variation of the refractive index with wavelength (nm) before and after irradiation with CO_2 laser (a) at Room temperature (b) 200 °C

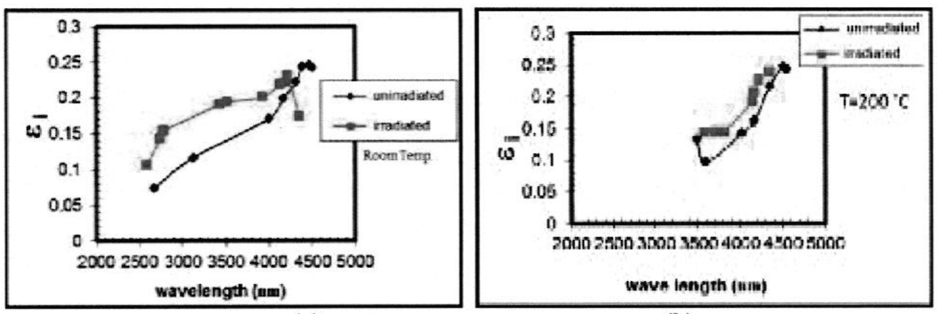
Figure (9) shows the real part of dielectric constant variation as a function of wavelength. It is shown that the real part of dielectric constant is gradually increased with increasing the wavelength until reaches high value then decreased as wavelength increase. The high value of the real part of dielectric constant indicates that the PbS films have ability to polarize. Also we note that the value of the real part of dielectric constant decreases after irradiation with CO_2 laser, and it is observed that the plot shape of ε_r as the same shape of n, that is because ε_r values depend on n , K values.



(a) (b)

Figure (9) The variation of real part of dielectric constant with wavelength (nm) before and after irradiation with CO_2 laser (a) at Room temperature (b) 200 °C

The imaginary part of dielectric constant (ε_i) various wavelength are shown in figure (10) , the behavior of ε_i is similar to α and K .



(a) (b)

Figure (10) The variation of The imaginary part of dielectric constant with wavelength (nm) before and after irradiation with CO_2 laser (a) at Room temperature (b) 200 °C

Conclusions

PbS thin films were prepared using thermal evaporation technique on glass substrate under vacuum equal to10^{-6} torr. The effects of irradiation by CO_2 laser on PbS thin films are :

1- Increase in the absorption value, absorption coefficient α, and the extinction coefficient K and imaginary part of dielectric constant .

2- Decrease in the transmittance T, reflectance R, the value of the energy gap E_g, refractive index n and in the real part of dielectric constant .

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دراسة الخواص البصريه لاغشية الرقيقه PbS قبل وبعد التشعيع بـليزر CO_2

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الملخص

تم في هذه الدراسة ترسيب اغشية رقيقة من مادة PbS على قواعد من الزجاج والمحضرة بطريقة التبخير الحراري الفراغي تحت ضغط (10^{-6} torr) وتم تلدين الاغشية بدرجة حرارة ($200C^{\circ}$) باستخدام فرن مفرغ من الهواء وبضغط (10^{-2}torr) وقد تم تشعيع العينات بليزر CO_2 ذو طاقة (1watt) وطول موجي (10.6µm) وعلى بعد (10Cm) من المصدر, ولمدة (5 sec) . ان دراسة الخواص البصرية للأغشية المحضرة قد تمت باستخدام مطياف IR . ومن خلال دراسة طيف النفاذية تم حساب الثوابت البصرية مثل الامتصاصية والانعكاسية ومعامل الامتصاص البصري (α) وفجوة الطاقة البصرية (E_g) ومعامل الخمود (K) ومعامل الانكسار (n) وثوابت العزل الكهربائي المعقد ($_{r}$ & $_{i}$) . وقد بينت النتائج ان التشعيع بالليزر ادى الى نقصان في النفاذيه والانعكاسية وطاقة الفجوة ومعامل الانكسار والجزء الحقيقي لثابت العزل بينما تزداد كل من الامتصاصيه ومعامل الامتصاص ومعامل الخمود والجزء الخيالي لثابت العزل في منطقة البحث .